DEVELOPMENT OF NEW METHOD FOR DISPERSING NANOFILLERS IN POLYCAPROLACTONE (PCL) NANOCOMPOSITE

SHAMINI A/P VESAYA KUMARAN

Thesis submitted in partial fulfilment of the requirements

for the award of the degree of

Bachelor of Chemical Engineering

Faculty of Chemical & Natural Resources Engineering
UNIVERSITI MALAYSIA PAHANG

JULY 2014

ABSTRACT

The consumption of plastic materials has been increasing and the accumulation of plastic at the end of its life cycle has also increased on the earth. This causes a big waste disposal and pollution problem. Therefore, this motivated many researchers to conduct studies to produce a polymer which is biodegradable and environmental friendly and at the same time has improved properties to produce plastics. Polymer nanocomposites have gained the greatest interest in this issue since few years. Polycaprolactone (PCL) as the polymer and Sodium montmorillonite (Na-MMT) a type of nanoclay as the inorganic nanofiller is used in this study. However, the polymer matrix and the nanoclay surface are not compatible because the inorganic Na-MMT is hydrophilic and PCL is hydrophobic. Thus, the main aim of this study is to develop a new modification method for dispersing the nanofiller into PCL nanocomposite and to fabricate PCL nanocomposite. The surface of Na-MMT was modified from inorganic to organic through surfactant method by reacting Aminopropylisooctyl Polyhedral Oligomeric Silsesquioxane (AP-POSS) surfactant with Na-MMT and the fabrication of PCL nanocomposite was then done through solution intercalation technique with both modified and unmodified nanoclay of different weight percentages. The structure and morphology of pure nanoclay, modified nanoclay (POSS-MMT) and the PCL nanocomposite were characterized by X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR) and Field Emission Scanning Electron Microscopy (FESEM). XRD revealed that the *d*-spacing of the POSS-MMT is increased by 0.64 nm as compared to Na-MMT. FTIR and FESEM results also showed that AP-POSS were well dispersed and intercalated throughout the interlayer space of Na-MMT. An exfoliated structure was also observed for PCL/POSS-MMT nanocomposite. Thermal properties of the nanocomposite were investigated using Differential Scanning Calorimetry (DSC) analysis which showed highest melting and crystallization temperature in PCL/POSS-MMT 5% nanocomposite which is 56.6˚C and 32.7˚C respectively whereas a lower degree of crystallinity for PCL/POSS-MMT nanocomposite as compared to PCL/Na-MMT nanocomposite and Thermogravimetric Analysis (TGA) recorded the highest degradation temperature in PCL/POSS-MMT 1% nanocomposite which is 394.1˚C at 50% weight loss ($T_{50\%}$) but a decrease in degradation temperature when POSS-MMT content is increased. Mechanical properties of the nanocomposite were analysed through tensile testing and the results indicated the highest Young's Modulus and tensile strength for PCL/POSS-MMT 3% nanocomposite which is 87 MPa and 2.64 MPa respectively while the lowest elongation at break in PCL/POSS-MMT 1% nanocomposite which is 138%. This study affords an efficient modification method to obtain organoclay with larger interlayer *d*-spacing to enhance the properties of polymer nanocomposite.

Keywords: Polymer nanocomposite, Polycaprolactone, Sodium montmorillonite, Modification of nanoclay, Aminopropylisooctyl Polyhedral Oligomeric Silsesquioxane (AP-POSS).

ABSTRAK

Penggunaan bahan plastik telah meningkat sejak kebelakangan ini serta akumulasi sisa plastik pada kitaran akhir hayatnya juga telah meningkat secara mendadak di atas permukaan bumi ini. Hal ini telah menyebabkan masalah pembuangan jumlah sisa yang besar dan juga masalah pencemaran. Oleh itu, situasi ini telah mendorong ramai penyelidik untuk menjalankan kajian bagi menghasilkan polimer yang terbiodegradasikan dan mesra alam sekitar berserta dengan penambahbaikan dalam ciri-cirinya supaya ia boleh digunakan untuk penghasilan bahan plastik. Polimer nanokomposit telah mendapat perhatian yang besar dalam isu ini sejak beberapa tahun. Polycaprolactone (PCL) sebagai polimer dan Sodium montmorillonite (Na-MMT) sejenis 'nanoclay' sebagai 'nanofiller' bukan organik telah digunakan dalam kajian ini. Walaubagaimanapun, matriks polimer dan permukaan 'nanoclay' tidak serasi antara satu sama lain kerana Na-MMT yang bukan organik adalah hidrofilik dan PCL organik adalah hidrofobik. Oleh itu, tujuan utama kajian ini adalah untuk menghasilkan satu kaedah pengubahsuaian baru untuk menyuraikan 'nanofiller' ke dalam PCL nanokomposit dan menghasilkan PCL nanokomposit. Permukaan Na-MMT telah diubah suai daripada bukan organik kepada organik melalui kaedah surfaktan dengan tindak balas surfaktan Aminopropylisooctyl Polyhedral Oligomeric Silsesquioxane (AP-POSS) bersama Na-MMT dan kemudian fabrikasi PCL nanokomposit melalui teknik interkalasi penyelesaian dengan 'nanoclay' tulen dan 'nanoclay' yang telah diubahsuai dengan peratusan berat yang berbeza. Struktur dan morfologi bagi 'nanoclay' tulen, 'nanoclay' yang diubahsuai (POSS-MMT) dan PCL nanokomposit telah dikaji melalui 'X-ray Diffraction Analysis (XRD)', 'Fourier Transform Infrared Spectroscopy (FTIR)' dan 'Field Emission Scanning Electron Microscopy (FESEM)'. Keputusan XRD menunjukkan bahawa jarak di antara lapisan dalam POSS-MMT telah meningkat sebanyak 0.64 nm berbanding Na-MMT. Kajian FTIR dan FESEM juga menunjukkan AP-POSS tersebar dan terinterkalasi dalam seluruh ruang lapisan Na-MMT. Struktur kelupas juga didapati untuk PCL/POSS-MMT nanokomposit. Ciri-ciri therma bagi nanokomposit yang telah dikaji melalui 'Differential Scanning Calorimetry (DSC)' yang menunjukkan suhu lebur dan penghabluran yang tertinggi bagi PCL/POSS-MMT 5% nanokomposit iaitu 56.6˚C dan 32.7˚C masing-masing manakala penurunan dalam darjah penghabluran yang lebih tinggi diperhatikan bagi PCL/POSS-MMT nanokomposit berbanding PCL/Na-MMT nanokomposit dan 'Thermogravimetric Analysis (TGA)' mencatatkan suhu degradasi yang tertinggi bagi PCL/POSS-MMT 1% nanokomposit iaitu 394.1˚C pada kehilangan berat 50% ($T_{50\%}$) tetapi penurunan dalam suhu degradasi didapati apabila kandungan POSS-MMT ditingkatkan. Ciri-ciri mekanikal untuk nanokomposit telah dianalisis melalui ujian tegangan dan keputusannya menunjukkan 'Young's Modulus' dan tegangan kekuatan yang tertinggi dalam PCL/POSS-MMT 3% nanokomposit iaitu 87 MPa dan 2.64 MPa masing-masing manakala pemanjangan pada putus yang paling rendah dalam PCL/POSS-MMT 1% nanokomposit iaitu 138%. Kajian ini mampu memberi kaedah pengubahsuaian yang baik untuk menghasilkan 'organoclay' dengan jarak di antara lapisan yang tinggi untuk meningkatkan ciri-ciri nanokomposit polimer.

Kata Kunci: Polimer nanokomposit, Polycaprolactone, Sodium montmorillonite, pengubahsuian 'nanoclay', Aminopropylisooctyl Polyhedral Oligomeric Silsesquioxane (AP-POSS).

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

SYMBOL	
PCL	Polycaprolactone
Na-MMT	Sodium Montmorillonite
PC	Polycarbonate
AP-POSS	Aminopropylisooctyl Polyhedral Oligomeric Silsesquioxane
XRD	X-Ray Diffraction
FESEM	Field Emission Scanning Electron Microscopy
FTIR	Fourier Transform Infrared Spectroscopy
TGA	Thermogravimetric Analysis
DSC	Differential Scanning Calorimetry
T_m	Melting Temperature
T_c	Crystallization Temperature
X_{cr}	Degree of Crystallinity
OMLS	Organically Modified Layered Silicates
PLA	Polylactic Acid
PA	Polyamide
OMMT	Organically Modified Montmorillonite
CL	Caprolactone
Zn-O	Zinc Oxide
PS	Polystyrene

PU	Polyurethane
TEM	Transmission Electron Microscopy
WAXD	Wide Angle X-Ray Diffraction
HDPE	High density Polyethylene
Bz	Benzimidazolium
PP	Polypropylene
PEO	Poly (oxyethylene)
PMMA	Poly (methyl metharcylate)
OAPS	octa (3-chloroammoniumpropyl) octasilsesquioxane
POSS-MMT	AP-POSS modified Na-MMT
C25A	Cloisite 25A
C30B	Cloisite 30B
PLLA	Poly ($_L$-lactide)
PBT	Polybutylene Terephthalate
CEC	Cation Exchange Capacity

CHAPTER 1

INTRODUCTION

1.1 **Background of Research**

Polymer nanocomposites have gained the greatest interest since few years. Polymer nanocomposite consists of inorganic nanofiller and organic polymers represent a new class of materials that exhibit improved performance compared to their microcomposite counterparts (Kango *et al.,* 2013). The improvements in many properties such as mechanical, thermal and barrier properties will be achieved at a very low loading of the inorganic nanofiller compared to conventional filled polymer. The properties of polymer nanocomposites depend on the type of inorganic nanofiller that are incorporated, their size and shape, their concentration and their interactions with the polymer matrix (Kango *et al.*, 2013).

Since the usage of plastic materials has been increasing lately, the accumulation of plastic at the end of its life cycle has also increased drastically on the earth. This causes a big waste disposal and pollution problem. This issue lead to the increasing environmental concerns of biodegradable and biocompatible synthetic polymers such as aliphatic polyester. Therefore, this motivated many researchers to conduct studies to produce a polymer nanocomposite which is biodegradable and environmental friendly in plastic industries. There are varieties of aliphatic polyesters that can be used in the

preparation of biodegradable polymer nanocomposites but the most intensity polymer is Polycaprolactone. Polycaprolactone (PCL) is a polymer synthesized chemically based on caprolactone units. PCL does not occur in nature but it is a very good biodegradable material in the packaging sector (Lepoittevin *et al.,* 2002a, b). The performance of the PCL can be improved by the addition of inorganic filler such as nanoclay in nanometer size (Luduena *et al.,* 2011). By adding small amount nanoclay into the polymer matrix will greatly enhance the mechanical, thermal, barrier and biodegradable properties, flammability, water adsorption as well as creep resistance of the polymer (Luduena *et al.,* 2011).

There are a lot of inorganic nanofiller available such as carbon nanofibers, carbon nanotube, nanosilica, exfoliated graphite (graphene), nanocrystalline metals, nanoaluminium oxide and nanotitanium oxide but then nanoclays gets a considerable interest among all other types of inorganic fillers because of its dimensional stability in two dimensions, good mechanical properties such as stiffness and strength and the most important factor is because it is a naturally abundant mineral which toxin free and biodegradable material (Chen and Evans, 2005). Studies on polyamide 11/clay nanocomposites have reported that the enhanced thermal stability is only achieved at very low loading level, thus making the obtained nanocomposites cheaper, lighter and easier to process than the conventional microcomposites (Liu *et al.,* 2003).

The nanoclays used in polymer nanocomposites field are mica, fluoromica, hectorite, fluorohectorite, saponite but of the greatest commercial interest is sodium montmorillonite (Na-MMT) that belongs to the structural family known as the 2:1 phyllosilicates (Leszcynska *et al.,* 2007). The efficiency of Na-MMT in improving the properties of polymer materials is related to both the strength of interactions between the nanoclay and polymer and the degree of dispersion in the polymer matrix (Goswami *et al.,* 2012). PC/MMT nanocomposites extruded by low and high shear extruders showed differences in structure (Stretz *et al.,* 2001).

An important issue to be considered during the preparation of polymer/clay nanocomposite is the compatibility of the polymer matrix and the inorganic nanoclay. Polymers are organophilic compound and they require organo-modified nanoclay to be used as filler so that better affinity between the filler and the matrix can be obtained (Corrales *et al.,* 2012). The hydrophilic nature of the nanoclay hinders homogenous dispersion of nanoclay in the polymer matrix (Gorrasi *et al.,* 2003). Nanoclays are actually having rich intercalation chemistry, therefore the surface of the nanoclay can be organically modified and made compatible with the organic polymer matrix. The nanoclay aggregation in the polymer is also one of the main problems with polymer nanocomposite. Na-MMT is a layered silicate whose interlayer ions can be exchanged by organic ions in order to produce an increment in the interlayer spacing (d_{001}) can improve the polymer/nanoclay compatibility (Gorrasi *et al.,* 2003). In order for the Na-MMT to be miscible with the polymer matrices the hydrophilic surface of the Na-MMT should be modified into an organophilic surface which results in increase of the interlayer *d*-spacing.

The modifications of Na-MMT with different methods have been investigated in many previous studies. The most common process is the ion-exchange reaction using cationic salts. There are some drawbacks in the modification by using ion exchange reaction such as low thermal stability of the cationic salts and the compounds are less readily intercalated in the polymer melts. However, in this study modification using the surfactant method will be considered. The surfactant method is a new approach developed to modify the surface of Na-MMT where the surfactant will be incorporated into the basal spacing of Na-MMT. This will increase the interlayer spacing of Na-MMT and helps in the interaction with the polymer chains. Surfactants are also quite a stable compound to be used in the polymer nanocomposite preparation. Surfactant method is expected to give a better surface modification for the Na-MMT and make it compatible with the polymer matrix.

The surfactant method will be done by modifying the inorganic nanoclay with a thermally stable surfactant which is Aminopropylisooctyl Polyhedral Oligomeric Silsesquioxane (AP-POSS). This AP-POSS surfactant can readily be intercalated into

the Na-MMT and this will cause an increase in the basal spacing of the nanoclay mineral (Wan *et al.,* 2008). The thermal and mechanical properties of the polymer nanocomposite can be improved by the addition of the AP-POSS surfactant into the interlayer space of the nanoclay mineral. AP-POSS also possesses a good biocompactibilty, recyclability and non flammability.

Polymer/clay nanocomposites usually can be prepared by using three different techniques such as in situ polymerisation of the monomers in the presence of the nanoclay, melt blending and solution intercalation. Therefore a lots of method been carried out to prepare polymer/clay nanocomposite. Microcomposite of polycaprolactone with MMT-Na^+ were obtained when they are prepared through melt blending (Gorrasi *et al.,* 2003). Exfoliated structure is obtained by in situ polymerization of ε-caprolactone with organically modified montmorillonite. By melt blending or by in-situ intercalative polymerization, intercalated nanocomposite can be obtained. Solution intercalation method will be considered in this study because only a small amount of polymer/clay nanocomposite is to be fabricated. Therefore, preparation of the PCL/clay nanocomposite under controlled environment can produce good composite materials.

1.2 Motivation

Polymeric materials are mainly used in the production of the plastic materials and packaging sector. The demand of plastic materials has been increasing among public however the degradation of the plastic material is a very big challenge today. This causes a serious waste management and environmental pollution problem. Therefore, this motivated to conduct this study to produce a polymer/clay nanocomposite which is environmental friendly, biodegradable and at the same time has improved properties to be used in many sectors such as packaging sector. However, the preparation of polymer nanocomposite requires modification of nanoclay surface as the

polymer matrix and nanoclay surface are not compatible. Therefore, the modification of the nanoclay surface has to be done prior to fabrication of the polymer/clay nanocomposite. PCL and nanoclay is motivated to be used in this study because PCL is biodegradable and nanoclay has environmental friendly properties.

1.3 Problem Statement

The polymer used in this study is PCL as it is a biodegradable polymer. However, it has low thermal and mechanical properties that can be overcome by preparation of PCL/clay nanocomposite. To produce a high performance polymer/clay nanocomposite several factors need to be considered. The polymer matrix and the nanoclay surface are not compatible. The surface of natural montmorillonite is hydrophilic while the polymer is hydrophobic in nature. Na-MMT is unsuitable for hosting non-polar organic molecules without prior treatment. In order to introduce the Na-MMT into the polymer material, the surface of Na-MMT has to be organically modified in advance. This should be done by increasing the interlayer spacing of the Na-MMT. By surface modification, the interlayer spacing of the nanoclay galleries can be increased and the miscibility of the Na-MMT with the polymer can be increased to achieve a good dispersion of layered structure within the polymer matrix.

1.4 Objective of Study

The objectives of this study are as follows

1) To modify the surface of sodium montmorillonite (Na-MMT) by using the surfactant method from inorganic to organic and study the interlayer *d*-spacing, structure and morphology of the organically modified Na-MMT.
2) To fabricate the PCL nanocomposite through solution intercalation technique and study the structure and morphology of fabricated PCL nanocomposite.
3) To study the thermal and mechanical properties of the fabricated PCL nanocomposite.

1.5 Scope of Study

The scopes of this study are as follows

1) To modify the surface of the sodium montmorillonite (Na-MMT) by using the surfactant method. The surfactant that will be used is Aminopropylisooctyl Polyhedral Oligomeric Silsesquioxane (AP-POSS).
2) To analyse the structure and morphology of the modified nanoclay by means XRD, FESEM and FTIR.
3) To fabricate the PCL nanocomposite through the solution intercalation technique and analyse its structure and morphology by means of XRD, FESEM and FTIR.
4) To study the thermal properties by using DSC and TGA and mechanical properties by tensile testing of the fabricated PCL nanocomposite.

1.6 Rationale and Significant

The ecosystem is disturbed and damaged as consequences of the non-degradable plastic materials for disposal items. The environmental impact of plastic wastes is increasing globally and alternative disposal ways are limited. The incineration of plastic wastes also produces a large amount of toxic product which will lead to global pollution. There is a very important need to develop environmental friendly polymer nanocomposite with improved properties to produce plastic materials. By this the accumulation of plastic wastes and biodegradation problem can be overcome. Accordingly, PCL is of increasing commercial interest since it is fully biodegradable favours this study and the nanofiller chosen which is a nanoclay (Na-MMT) is also an environmental friendly material.

Therefore a good biodegradable polymer nanocomposite can be produced to be used in packaging sector. The main problem regarding this study is the Na-MMT and the PCL polymers are not compatible. Therefore, a suitable surface modification of the Na-MMT should be carried out in order to increase the interlayer space of the Na-MMT galleries and make it compatible with the polymer matrix. The surfactant method will be used here as the ion exchange method has been already established and there are many studies conducted regarding the ion exchange method. The properties of the PCL/ Na-MMT nanocomposite can be improved through modifying the surface of Na-MMT by using surfactant, Aminopropylisooctyl Polyhedral Oligomeric Silsesquioxane (AP-POSS).

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction to Polymer Nanocomposite

Polymer Nanocomposite has gained a great interest of many in scientific and technological field. There has been a strong emphasis in the development of polymer nanocomposites for the last 20 years. At least one of the materials is with nanometer dimension and with nanometer scale of less than 100 nm. The nanocomposite technology has developed an efficient and powerful strategy to upgrade the structural and functional properties of pure polymers. The materials that produced will be stronger and lighter compared to pure polymer. Polymer nanocomposites are of lower density and have an easy processability. A polymer nanocomposite is made up of polymer and synthetic or natural inorganic nanofiller. Using small amount of nanofiller in the polymer resins gives a good improvement of many properties such as thermal, mechanical, barrier and flame retardancy to the polymer nanocomposite. Under the optimum conditions, these property improvements result from only 2% to 5% addition of the dispersed nanophase (Goswami *et al.,* 2012). Dispersion of inorganic filler within the polymer matrix is the main reason for the enhancement of those properties.

The properties of the polymer nanocomposite however are affected by the nature, content and properties of the nanofiller, dimension of the nanofiller and interfacial interaction between matrix and the nanofiller. Recent interest in polymer matrix based nanocomposites has emerged initially with interesting observations involving exfoliated nanoclay and more recent studies with carbon nanotubes, carbon nanofibers, exfoliated graphite (graphene), nanocrystalline metals and a host of additional nanoscale inorganic filler or fiber modifications (Paul and Robeson, 2008).

Polymer nanocomposites especially polymer-layered silicate nanocomposites, represent a good replacement to conventionally filled polymers because of the dispersion of nanometer-size silicate sheets (Pinnavaia *et al.,* 2000). Polymer nanocomposites based on layered silicates are of recent interest because of the fundamental questions they address and potential technological applications (Viville *et al.,* 2003). They have the potential of being a low-cost alternative to high-performance composites for commercial applications in both the automotive and packaging industries (Nguyen *et al.,* 2006). Polymer clay nanocomposites also have gained a great interest since the first report prepared by the Toyota research group (Okada *et al.,* 1990).

2.2 Biodegradable Polymers

Plastics are ideal for many applications such as in packaging, building materials and commodities but it can lead to waste disposal problems as these materials are not readily biodegradable and they accumulate in the environment. Even though recycling is an environmentally attractive solution for this problem, only a small portion of plastics is recycled and most of these wastes end up in municipal burial sites (Wu, 2003). Landfill sites are very limited and disposal of these wastes in incineration leads to the production of toxic products that lead to environmental pollution. Therefore, best solution to overcome this issue is by the development of biodegradable polymer or

green polymer material to produce plastics (Eili *et al.,* 2012). A reduction in the volume of waste and compostability in the natural cycle, complete biological degradability and protection of the climate through the reduction of the amount of carbon dioxide released is the reasons why biodegradable polymer is required.

Biodegradable polymers are those environment friendly polymers that can be hydrolytically or enzymatically degraded after a limited time of exposure to humidity, light or microorganism without releasing any toxic products to the environment (Umare *et al.,* 2007). Majority of biodegradable polymers have excellent properties that can be compared with many non-biodegradable fossil-fuel based commodity polymers which are now rapidly entering main-stream uses (Sinha *et al.,* 2005). Renewable resources based biodegradable polymers are competing well with the non-biodegradable fossil-fuel based commodity polymers and because of this situation, the annual sales growth rate of biodegradable polymers is more than 20% (Mohanty *et al.,* 2002).

Aliphatic polyesters are the main category of biodegradable polymer. In recent years, aliphatic polyesters are a growing in research issues as they appear to be a solution to the emerging environmental concerns that have risen due to their biodegradability. They are biopolymers where the repeating units are bonded via ester linkages with many kinds of esters are present in nature and enzymes that degrade them. (Bikiaris, 2011). The aliphatic polyesters considered to be the only high molecular weight biodegradable compounds and their hydrolysable ester bonds make them biodegradable. A number of companies produce biodegradable aliphatic polyesters that produce biodegradable plastics on a commercial scale.

Polylactic acid (PLA), polybutylene succinate (PBS), polybutylene adipate (PBA) and poly (ε-caprolactone) (PCL) are members of this group which are naturally biodegradable material. They are considered to be good biodegradable polymers because of their low production cost and easy processibility in large scale production. The biodegradable polymers have good commercial potential for plastics but some of the properties such as low heat distortion temperature, brittleness, high gas permeability

and low melt viscosity for further processing restrict their use in a wide-range of applications (Sinha *et al.,* 2005). Therefore these properties can be improved through the preparation of nanocomposite with nanofiller such as nanoclay. The effect of the nanofiller on the biodegradability of aliphatic polyesters has been an interesting aspect of the research in the field of polymer nanocomposites. The research on the biodegradability of the PCL nanocomposite and PLA nanocomposites showed a significant improvement of the biodegradability and properties of the neat PCL and PLA.

2.3 Polycaprolactone (PCL)

Polycaprolactone best suits this studies because it is a type of biodegradable polyester. PCL is a type of polymer fabricated from the polymerization of non-renewable raw materials such as crude oil. Polycaprolactone (PCL) is a polymer synthesised chemically by using ε-caprolactone units. There are two main ways to synthesis polycaprolactone which is the polycondensation of a hydroxycarboxylic acid (6-hydroxyhexanoic acid) and the ring-opening polymerisation (ROP) of a lactone (epsilon-caprolactone (epsilon-CL)). PCL can be prepared through ring opening polymerization of ε-caprolactone unit using catalyst such as stannous octoate. PCL is a hydrophobic and semi-crystalline polymer that could be thermally formed.

Although PCL does occur in nature, it is a fully biodegradable polymer compared to other types of polymer. Poly (ε-caprolactone) (PCL) is an important biodegradable material in degradable packaging applications (Lepoittevin *et al.,* 2002a, b). PCL is commonly used for polyurethane applications such as polyols and also used as PVC solid plasticizer. PCL is also normally used as a compatibilizer or as a soft block in polyurethane formulations. It also finds some applications based on its biodegradable character in domains such as biomedicine and environment. Enzymes and fungi also expected to easily biodegrade PCL material. PCL has melting

temperature of about 60˚C and a glass transition temperature of about -60˚C. It has a density of 1.145 g/cm^3. PCL is a quite cheap material compared to other materials that are used in the market and the fabrication method is also easy to be done. PCL is a soluble polymer in various solvent and it is a semi-rigid material at room temperature.

Therefore, it can be easily reacted with many other solvent or compound. It also has a high elongation at break which is more than 700%. The biodegradability, high strength and high modulus of PLA make it a good material for many application but its applications are limited due to its brittleness and non-flexibility, high crystallinity, slow degradation and costliness compared to PCL (Li *et al.*, 2009). PCL is regarded as a soft and hard tissue compatible bio-resorbable material, and it has been considered as a potential substrate for wide applications (Corrales *et al.*, 2012).

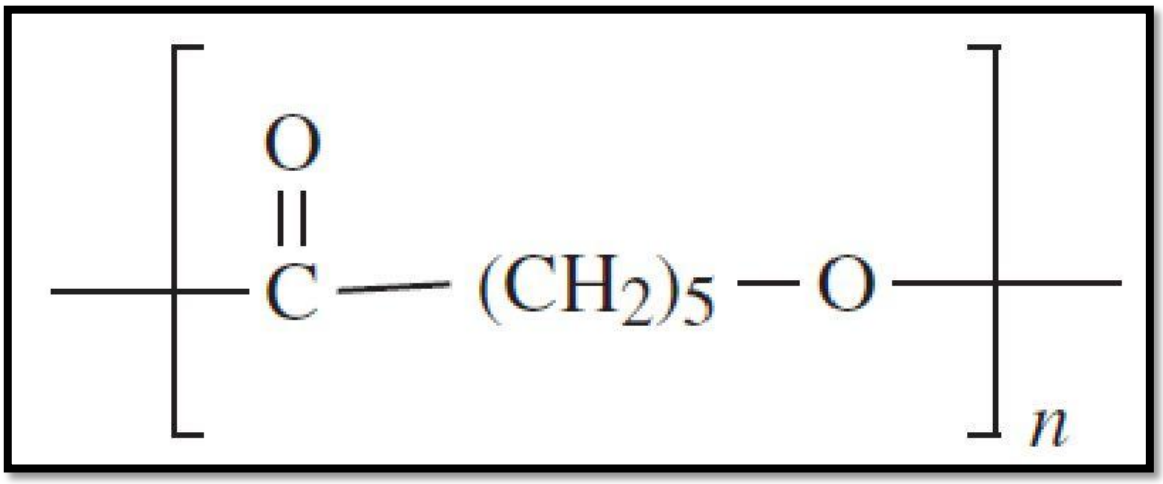

Figure 2.1: Polycaprolactone (PCL) (Ghanbarzadeh and Almasi, 2013)

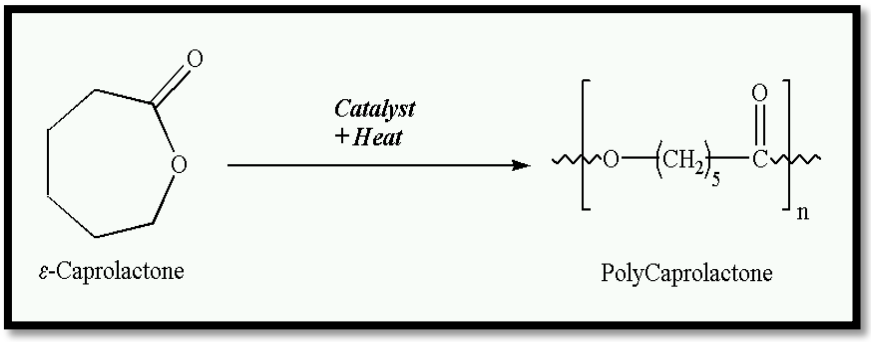

Figure 2.2: Formation of Polycaprolactone

(Source: www.absoluteastronomy.com)

2.4 Polycaprolactone (PCL) Nanocomposite

The major drawback of PCL is its low thermal and mechanical properties which can be overcome by preparation of PCL nanocomposite. Performance of the PCL can be enhanced through addition of a small amount inorganic filler of nanometer-size. This is the kind of material called polymer nanocomposite. The PCL based nanocomposites is the first biopolymer nanocomposite prepared by in-situ intercalative polymerization method which was done by Messersmith and Giannelis in 1993 where they used fluorohectorite (FH) for the synthesis of nanocomposite. The intercalation of the CL monomer was revealed by powder XRD which shows an increase in the silicate *d*-spacing from 1.28 to 1.46 nm (Messersmith and Giannelis, 1993). PCL nanocomposite also were prepared by a synthetic procedure for nylon 6/OMLS nanocomposite where in its most basic form it involves dispersion of OMLS in an organic monomer followed by polymerization of the monomer (Messersmith *et al.,* 1995). PCL/layered silicate nanohybrid has also been synthesized by ring opening polymerization of CL according to a well-controlled coordination–insertion mechanism (Lepoittevin *et al.,* 2002).